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Motor Vehicle Emissions under Reduced Ambient Temperature Idle Operating Conditions (Journal Version)

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16. ABSTRACT

Gasoline motor vehicle organic emissions are elevated by reduced ambient temperature operating conditions, and the practice of warming vehicles with extended idle periods is common during winter months. Total hydrocarbon, carbon monoxide, nitrogen oxides, and formaldehyde emissions are examined under idle operation at 20°F, 40°F, and 68°F with six gasoline fueled vehicles (including noncatalyst, early catalyst, and late model catalyst) and a methanol fueled prototype vehicle. The emissions were substantially reduced by the late model catalyst control technologies at all temperature examined. Formaldehyde emissions were elevated with methanol fuel.

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MOTOR VEHICLE EMISSIONS UNDER REDUCED AMBIENT TEMPERATURE IDLE OPERATING CONDITIONS

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Abstract—During winter months, motor vehicles are typically operated with extended preliminary idle periods. Total hydrocarbon, carbon monoxide, nitrogen oxides and formaldehyde emissions are examined under idle operation at 20, 40 and 68°F with six gasoline fueled vehicles (including non-catalyst, early catalyst and late model catalyst) and a methanol-fueled prototype vehicle. The emissions were substantially reduced by the late model catalyst control technologies at all temperatures examined. Formaldehyde emissions were elevated with methanol fuel.

Key word index: Motor vehicle emissions, idle operation, temperature sensitivity, formaldehyde.

INTRODUCTION

Emissions from motor vehicle engines are sensitive to many operating conditions, including speed, load, ambient temperature and fuel composition. Several investigators have observed that gasoline engine organic and CO emission rates are elevated by reduced ambient temperatures, especially so under cold start operation (Miles and Homfeld, 1974; Robertson, 1974; Ashby *et al.*, 1974; Heinmiller, 1978; Eccleston and Hurn, 1978; Ostrouchov, 1979; Spindt and Hutchins, 1979; Chang *et al.*, 1980; Marshall and Eccleston, 1980; Bruetsch, 1981; Braddock, 1981; Austin *et al.*, 1983). Diesel engine emissions are not so sensitive to ambient temperature (Braddock, 1982). Most published data identify organic emissions only in terms of total hydrocarbon (THC) emission rates as determined by flame ionization detection (FID) analytical procedures. Little is known of the composition of the organic emissions elevated by winter driving conditions. Because of growing interest in population exposure to toxic air pollutants, a program has been undertaken to determine the emission rates of formaldehyde, benzene and other individual organics using laboratory simulations of winter driving conditions. Initial program emphasis is being directed to formaldehyde, expanding the data base on which Federal regulatory decisions can be made (Federal Register, 1984a, b, 1985, 1986). Formaldehyde emissions have also been of special interest to those advancing methanol-fueled engine technologies (Harvey *et al.*, 1984).

This communication describes efforts to define sampling procedures suitable for formaldehyde at reduced ambient temperatures, procedures which are complicated by the potential for condensed water in the exhaust transfer tubing. Organic emissions are most sensitive to ambient temperature under cold start conditions, and vehicles are commonly operated with extended idle periods during winter months. Therefore, preliminary efforts in this program emphasized idle operation. Future efforts will comprehensively examine organic emissions, providing emission factors for about 200 individual HC and oxygenated HC compounds as a function of ambient temperature.

METHODS

A general overview of the scope of this study is provided in Table 1. Six gasoline-fueled automobiles and one methanol-fueled prototype vehicle were examined with cold and hot start idles at 20, 40 and 68°F. Each vehicle was also examined with standard certification Federal Test Procedure (FTP) transient urban cycles at 68°F (Code of Federal Regulations, 1983). Three of the test vehicles, the 1972 Impala, 1977 Mustang and 1983 Methanol Escort were Government owned. The remainder of the test vehicles were borrowed from the local consumer fleet. No attempts were made to optimize any of the vehicles for low emissions. All had satisfactory driveability as received. The methanol-fueled Escort was an early generation prototype with 16,000 miles (25,000 km) of fleet service. The catalyst was not optimized for low emissions with methanol fuel and may not be representative of current methanol fuel technology. Of necessity, summer and winter grade fuels (varying volatility) were used in this program. Driveability at 20°F required

Table 1. Study parameters

Test vehicles	Catalyst type	Odometer	Test fuels
1970 Chevrolet Nova	None	181,000	Unleaded gasoline
1972 Chevrolet Impala	None	24,000	Unleaded gasoline
1977 Ford Mustang	Oxidation	37,000	Unleaded gasoline
1978 Toyota Celica	Oxidation	79,000	Unleaded gasoline
1985 Chevrolet Celebrity	3-Way	14,000	Unleaded gasoline
1985 Ford Tempo	3-Way	24,000	Unleaded gasoline
1983 Ford Escort	3-Way, open loop	16,000	85% methanol–15% unleaded gasoline
Temperatures studied: 20°F, 40°F, 68°F			
Driving modes: cold idle, hot idle, FTP (68°F)			
Emissions measured: HCHO, THC, CO, NO_x, MeOH			
Fuel RVP values: unleaded gasoline; winter 14.9, summer 11.4: methanol fuel; winter 8.8, summer 8.4			

higher volatility fuels. The summer grade fuels were satisfactory at 40 and 68°F. The methanol fuels were prepared by blending 15 volume % of the winter and summer grade unleaded gasolines with methanol.

THC, CO and NO_x measurements were made using analytical procedures prescribed for emissions certification. Methanol emissions (from the prototype vehicle) were determined using previously described procedures involving water-impinger collection with gas chromatographic analysis (Urban, 1983). Formaldehyde measurements were completed using procedures previously described by Tejada (1986). Dinitrophenylhydrazine (DNPH) coated silica cartridges were used to collect formaldehyde from the diluted exhaust. Tejada has demonstrated that the DNPH cartridge collection procedure in association with high performance liquid chromatography (HPLC) analysis can be used for sensitive, accurate determination of formaldehyde in dilute automobile exhaust. The silica cartridges are commercially available (Part No. 51900, Waters Associates, Milford, MA). Briefly, preparation of the cartridges for formaldehyde sampling involved a preliminary wash with high purity acetonitrile (ACN), followed by a 5 ml wash with acidified (10 drops concentrated HCl per 150 ml DNPH solution) 3% DNPH solution in ACN. The coated cartridges are then dried with nitrogen and stored until used (up to 2 months) under refrigeration in glass-stoppered bottles. Collected samples can be similarly stored for 2 weeks without compromising sample integrity.

The THC measurements with the methanol-fueled prototype were corrected for FID response to methanol. That is, the FID analyzer output was adjusted for sample methanol concentration (determined by gas chromatography) so that THC mass calculations were based only on the hydrocarbon components of the exhaust.

Winter driving conditions were simulated by enclosing the vehicle and chassis dynamometer in a thermostatically-controlled cold cell with exhaust handling equipment as depicted in Fig. 1. The exhaust was quantitatively transferred from the vehicle to a standard Constant Volume Sampling (CVS) system (Code of Federal Regulations, 1983), located outside of the cold cell, using a 20 ft by 3 in. diameter 110°C heated sample line (Conrad, Co., Columbus, OH). The quantitative transfer and collection of formaldehyde was

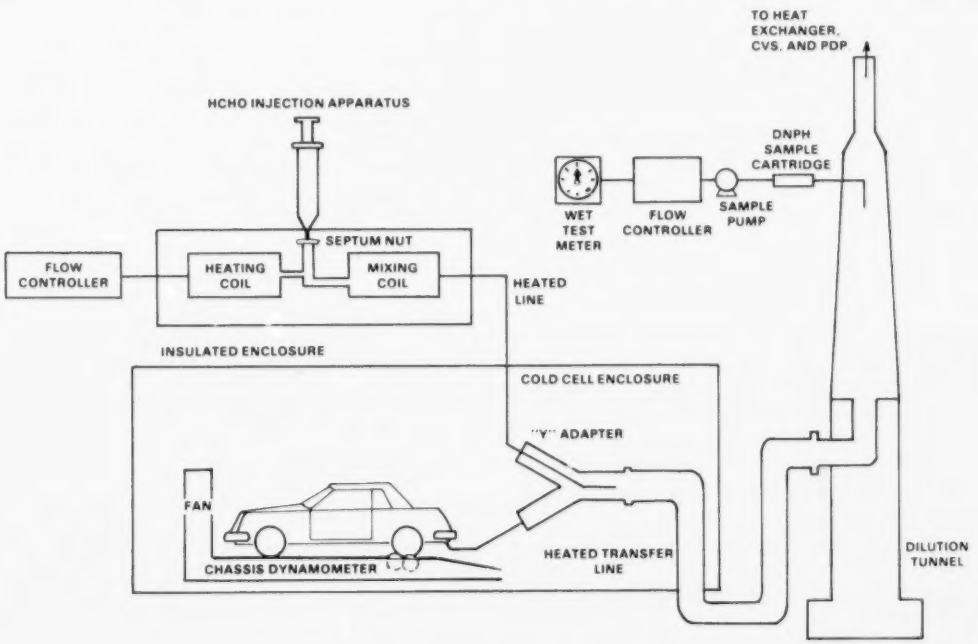

Fig. 1. Test cell configuration.

Table 2. Idle emissions

Test vehicles	Temp. (°F)	Cold start THC (g min^{-1})	CO (g min^{-1})	NO_x (g min^{-1})	HCHO (mg min^{-1})	Hot start THC (g min^{-1})	CO (g min^{-1})	NO_x (g min^{-1})	HCHO (mg min^{-1})
Non-catalyst									
1970 Chev. Nova	20	2.26 ± 0.40	67.0 ± 17.5	0.08 ± 0.04	22.8 ± 4.9	0.96 ± 0.14	49.6 ± 3.5	0.02 ± 0.01	9.9 ± 1.6
	40	2.12 ± 0.34	60.1 ± 7.8	0.06 ± 0.03	22.9 ± 4.1	1.65 ± 0.05	42.2 ± 1.7	0.11 ± 0.01	25.9 ± 2.2
	68	1.79 ± 0.38	49.0 ± 4.7	0.03 ± 0.04	15.9 ± 6.7	0.89 ± 0.07	42.9 ± 3.8	0.03 ± 0.003	9.0 ± 0.5
1972 Chev. Impala	20	29.0 ± 9.9	91.4 ± 21.1	0.05 ± 0.02	68.9 ± 7.5	2.64 ± 1.6	17.6 ± 8.0	0.05 ± 0.004	14.5 ± 2.8
	40	24.6 ± 7.5	56.5 ± 8.6	0.03 ± 0.01	49.6 ± 12.2	1.90 ± 1.3	16.9 ± 9.3	0.05 ± 0.01	15.8 ± 4.1
	68	3.86 ± 2.51	52.3 ± 33.6	0.03 ± 0.01	29.6 ± 16.7	0.77 ± 0.04	14.8 ± 13.9	0.04 ± 0.003	12.1 ± 1.1
Oxidation catalyst									
1977 Ford Mustang	20	57.3 ± 19.9	81.8 ± 14.8	0.07 ± 0.04	37.4 ± 27.1	4.82 ± 1.6	18.0 ± 4.3	0.04 ± 0.03	2.9 ± 1.7
	40	38.0 ± 16.3	85.5 ± 14.5	0.04 ± 0.02	50.2 ± 29.2	1.86 ± 0.6	5.3 ± 2.0	0.03 ± 0.004	14.3 ± 7.2
	68	19.4 ± 15.9	43.9 ± 24.6	0.02 ± 0.01	37.5 ± 18.1	1.78 ± 0.14	26.6 ± 2.6	0.01 ± 0.004	14.2 ± 1.3
1978 Toyota Celica	20	0.42 ± 0.16	25.0 ± 6.9	0.09 ± 0.02	18.5 ± 9.0	0.04 ± 0.003	2.7 ± 0.3	0.01 ± 0.006	5.3 ± 0.4
	40	0.21 ± 0.06	15.0 ± 2.6	0.06 ± 0.01	9.4 ± 2.2	0.07 ± 0.004	2.9 ± 1.8	0.03 ± 0.05	7.5 ± 4.8
	68	0.10 ± 0.04	3.0 ± 0.3	0.09 ± 0.08	7.8 ± 1.4	0.06 ± 0.01	3.3 ± 0.3	0.01 ± 0.001	7.0 ± 0.6
3-Way catalyst									
1985 Chev. Celebrity	20	0.42 ± 0.06	7.4 ± 1.4	0.06 ± 0.01	4.5 ± 0.9	0.08 ± 0.04	0.38 ± 0.29	0.01 ± 0.01	1.4 ± 1.2
	40	0.29 ± 0.03	5.1 ± 0.2	0.04 ± 0.01	3.6 ± 0.2	0.11 ± 0.06	0.47 ± 0.38	0.02 ± 0.01	1.4 ± 1.3
	68	0.17 ± 0.03	0.6 ± 0.2	0.01 ± 0.01	6.6 ± 2.0	0.08 ± 0.06	0.27 ± 0.23	0.01 ± 0.01	1.0 ± 0.9
1985 Ford Tempo	20	0.60 ± 0.05	9.2 ± 0.7	0.20 ± 0.02	9.2 ± 1.2	0.35 ± 0.03	0.24 ± 0.02	0.02 ± 0.01	9.9 ± 2.1
	40	0.44 ± 0.02	3.4 ± 0.7	0.14 ± 0.03	1.9 ± 1.1	0.31 ± 0.03	0.22 ± 0.04	0.02 ± 0.01	12.8 ± 1.8
	68	0.93 ± 0.09	3.4 ± 0.2	0.08 ± 0.01	12.3 ± 2.5	0.32 ± 0.15	0.35 ± 0.04	0.02 ± 0.01	8.5 ± 3.5
Methanol proto.									
1983 Ford Escort	20	1.14 ± 0.14	17.4 ± 2.3	0.12 ± 0.03	82.1 ± 24.9	0.94 ± 0.17	7.1 ± 0.8	0.05 ± 0.02	56.4 ± 13.0
	40	0.31 ± 0.11	12.1 ± 4.4	0.12 ± 0.02	76.9 ± 26.3	0.27 ± 0.08	5.1 ± 2.9	0.02 ± 0.01	34.6 ± 5.1
	68	0.08 ± 0.04	3.8 ± 1.3	0.08 ± 0.04	50.1 ± 6.8	0.14 ± 0.02	2.2 ± 1.3	0.02 ± 0.01	32.8 ± 7.2

Note: Ford Escort MeOH emission : 20(°F) 3.63 ± 0.41 (g min^{-1}) 20(°F) 1.74 ± 0.65 (g min^{-1})
40 0.85 ± 0.48 40 0.32 ± 0.03
68 0.26 ± 0.12 68 0.11 ± 0.06.

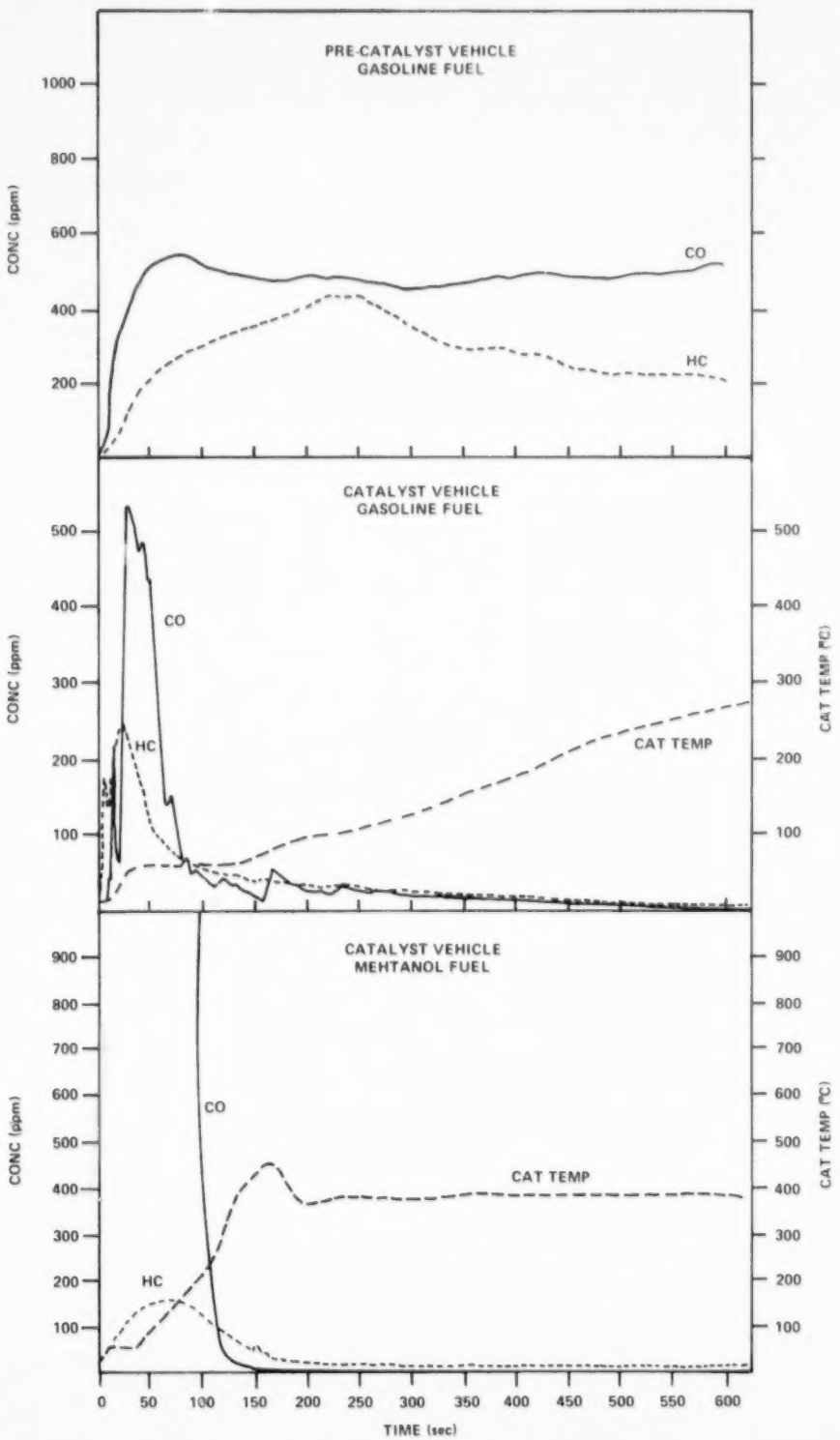

Fig. 2. Real-time emission traces for cold start 10-min idle periods.

verified under all operational conditions of this study by means of calibrated injections of known amounts of formaldehyde (concentrations similar to tailpipe levels) into the transfer system at the tailpipe connection as shown in Fig. 1. The calibrated injections were achieved by flash vaporization and nitrogen dilution of motor driven syringe injections of 37% formalin solution (Fisher Scientific). The injections were into the stabilized exhaust of an idling automobile. It was observed that the injected formaldehyde could be collected with an efficiency of 95% ± 5% ($N = 6$) considering the established formaldehyde level in the stabilized auto exhaust. Without the heated transfer line, less than 50% of the injected formaldehyde was collected at 20°F, and the results were highly erratic.

The test sequence with each vehicle included an overnight soak at the selected temperature, followed by a 10-min cold start idle test and a series of five 10-min hot start idle tests at the selected temperature. Separate formaldehyde cartridges were collected for each 10-min period. The sequence was repeated until a minimum of 10 replicates of each condition were completed. A minimum of two FTP transient tests were also completed with each vehicle at 68°F.

RESULTS AND DISCUSSION

A concern in using the 110°C heated transfer line between the vehicle and the CVS system was that water condensing in the tailpipe would absorb formaldehyde which would subsequently be released to the gas phase in the transfer line, in contrast to dripping on the driveway and not being immediately released during actual winter idle periods. To examine this possibility, the exhaust handling system was fitted with a water collection device at the end of the tailpipe immediately before the heated line. The tailpipe condensed water was collected and found to contain 18.9 ± 3.8% ($N = 4$) of the total emitted formaldehyde at 20°F. The formaldehyde emission rates reported in this paper comprise both the gas phase and that which is water absorbed.

Table 2 provides cold start and hot start idle THC, CO, NO_x and formaldehyde emission rates for all vehicles and test conditions examined. It is important to note that the emission rates are reported in terms of mass min^{-1} for 10-min sampling periods. Real time (0.1 s time resolution) measurements of THC and CO concentrations and catalyst temperature (if test vehicles were catalyst equipped) were completed to permit observation of emission rate changes during the 10-min sampling period. Typically, HC and CO emissions stabilized after 2–3 min with the catalyst equipped vehicles (including the methanol-fueled vehicle) and remained elevated and unstable after 10 min with the non-catalyst configurations. Figure 2 presents representative traces. With the catalyst vehicles, 10-min sample integration periods gave lower g min^{-1} emission rates than would be obtained with 5-min sample integration periods. This should be considered when comparing results with other studies. The NO_x emission rates were low from all vehicles at all temperatures because of the low engine loads associated with idle operation.

Attempts to correlate variable temperature, idle operation formaldehyde emissions with HC emissions were not productive. R-square values of 0.7–0.8 were observed with regression analysis, after elimination of high HC emission outliers. The idle formaldehyde emission rates were substantially reduced by the late-model catalyst technologies examined, and were higher from the methanol prototype vehicle than from any of the gasoline-fueled vehicles examined. Idle formaldehyde and HC emission rates did not vary predictably with temperature. This could result in part from the varied designs for low temperature fuel enrichment and from the necessity to operate with different fuel volatilities at 20 and 40–68°F. Linear regression analysis of the 68°F FTP transient emission rates reported in Table 3 (excluding the Mustang data) indicated a coefficient of correlation of formaldehyde emissions with HC emissions of 0.95. However, with the limited test fleet size and a positive y-intercept (8.3 mg mi^{-1}) exceeding the formaldehyde emission rates observed with the 1985 3-way catalyst vehicles, one should be guarded at attempting to project formaldehyde emissions from observed THC emissions. As with the idle emissions, the transient formaldehyde emissions were

Table 3. FTP emissions (68°F)

Test vehicles	THC (g mi^{-1})	CO (g mi^{-1})	NO_x (g mi^{-1})	HCHO (mg mi^{-1})
Non-catalyst				
1970 Chev. Nova	7.37 ± 1.18 (4.1)	131 ± 10 (34)	1.48 ± 0.07	110 ± 0.3
1972 Chev. Impala	6.74 ± 0.23 (3.0)	162 ± 10 (28)	1.23 ± 0.08 (3.1)	95.7 ± 0.3
Oxidation catalyst				
1977 Ford Mustang	7.33 ± 1.76 (1.5)	75.2 ± 9.5 (15)	3.03 ± 1.57 (2.0)	10.9 ± 0.8
1978 Toyota Celica	1.22 ± 0.15 (1.5)	11.2 ± 0.7 (15)	1.56 ± 0.07 (2.0)	42.9 ± 0.2
3-Way catalyst				
1985 Chev. Celebrity	0.14 ± 0.01 (0.41)	2.16 ± 0.21 (3.4)	0.21 ± 0.01 (1.0)	3.97 ± 0.17
1985 Ford Tempo	0.31 ± 0.02 (0.41)	6.85 ± 0.59 (3.4)	0.79 ± 0.05 (1.0)	3.74 ± 0.01
Methanol proto.				
1983 Ford Escort	0.49 ± 0.15 (0.41)	6.93 ± 1.04 (3.4)	0.64 ± 0.06 (1.0)	113 ± 34

Note: Ford Escort MeOH emissions: 0.96 ± 0.15 g mi^{-1}; numbers in parentheses indicate new car Federal emission standards for the indicated model year.

lower from the late model catalyst vehicles than the precatalyst vehicles, and elevated from the methanol vehicle. The THC and CO emission rates presented in Table 3 for the non-catalyst vehicles and the 1977 Mustang, when compared with the indicated model year Federal Emission Standards, suggest that these vehicles were experiencing some malfunction condition. As previously indicated, the driveability of each was satisfactory.

A notable difference in emissions from the methanol-fueled Escort and the late-model catalyst equipped gasoline vehicles is formaldehyde, with the methanol vehicle about an order-of-magnitude higher. A similar observation was made by Gabele *et al.* (1985). Of course with methanol fuel, a substantial fraction of the total tailpipe organic emissions is methanol. It is interesting to note however, that although the fuel used with the methanol vehicle included only 15% gasoline, HC emission exceeded that from the late model catalyst vehicles under some of the test conditions. This may be associated with the relatively low volatility of the methanol fuels and/or cold start fuel enrichment control.

It can be concluded that motor vehicle idle operation organic emissions vary significantly among control and engine technologies, with the emission rates substantially reduced by functioning catalyst systems. Formaldehyde emissions are elevated by methanol fuel. With some vehicles a predictable idle operation temperature sensitivity was indicated, with others it was not. The data suggest that one should be guarded when attempting to predict formaldehyde emissions from observed THC emissions.

Continuing efforts will determine the emission rates of over 200 HC and oxygenated HC compounds. Both idle operation and urban transient driving simulations will be examined at 20, 40 and 68°F.

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